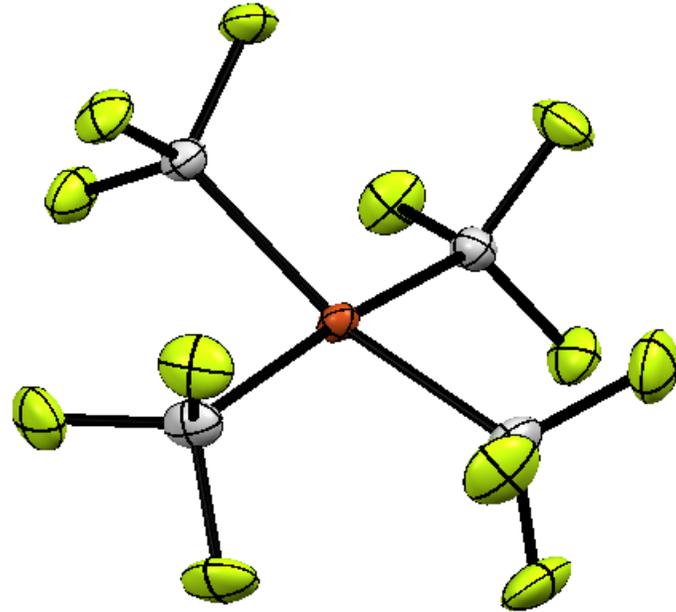
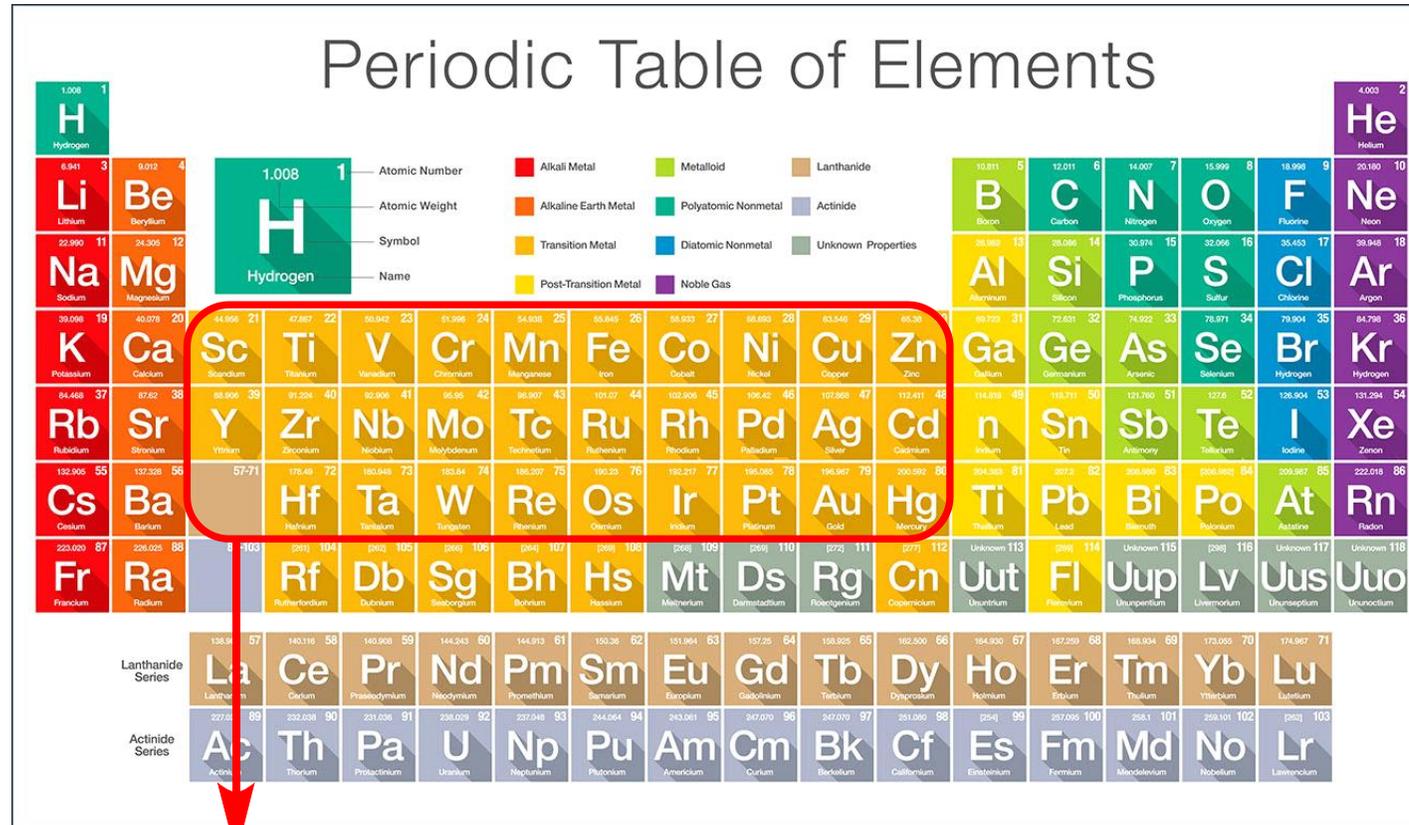


Inverted Ligand Field Theory



Literature Group Meeting
Grayson Ritch
June 8, 2018

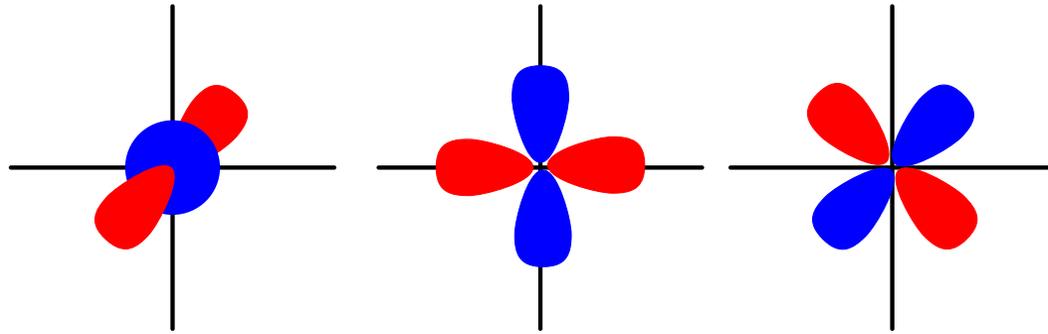
d-Block Metals



d-block metals

- valance orbitals are *d*-orbitals
- 5 degenerate *d*-orbitals that can hold $2e^-$ each for a total of $10e^-$
- d*-orbitals differ in their 3-D orientation

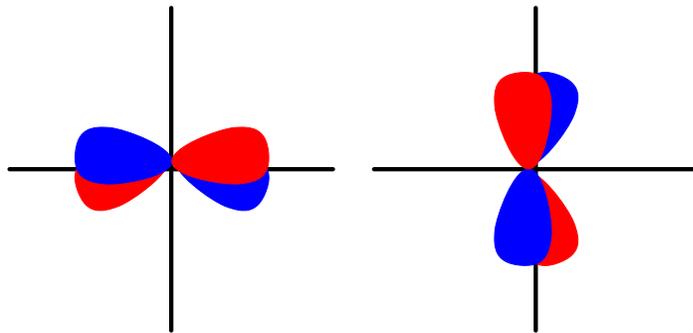
The *d*-orbitals



dz^2

dx^2-y^2

dxy



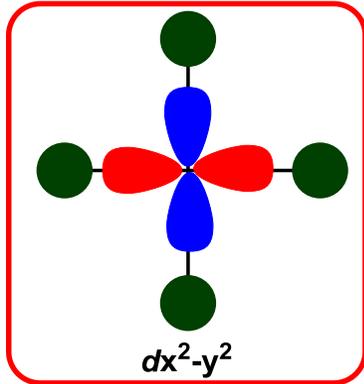
dxz

dyz

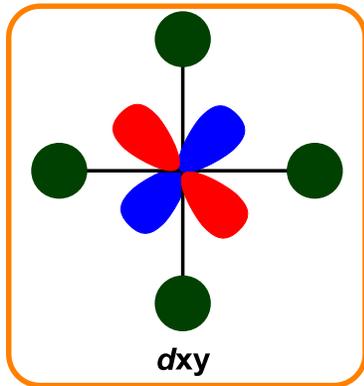
-5 degenerate (same energy) orbitals in the absence of a ligand environment

-Introduction of a ligand field perturbs the energy of each orbital differently depending on the geometry of the ligand field

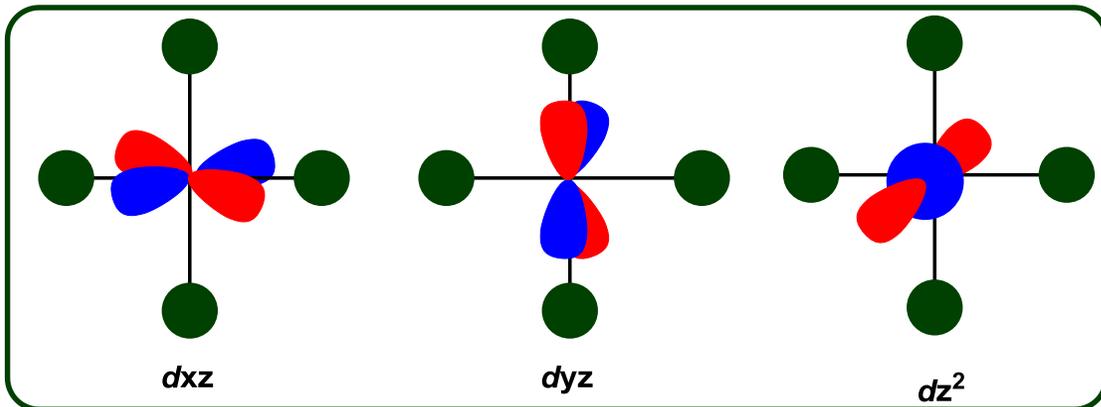
Crystal Field Splitting



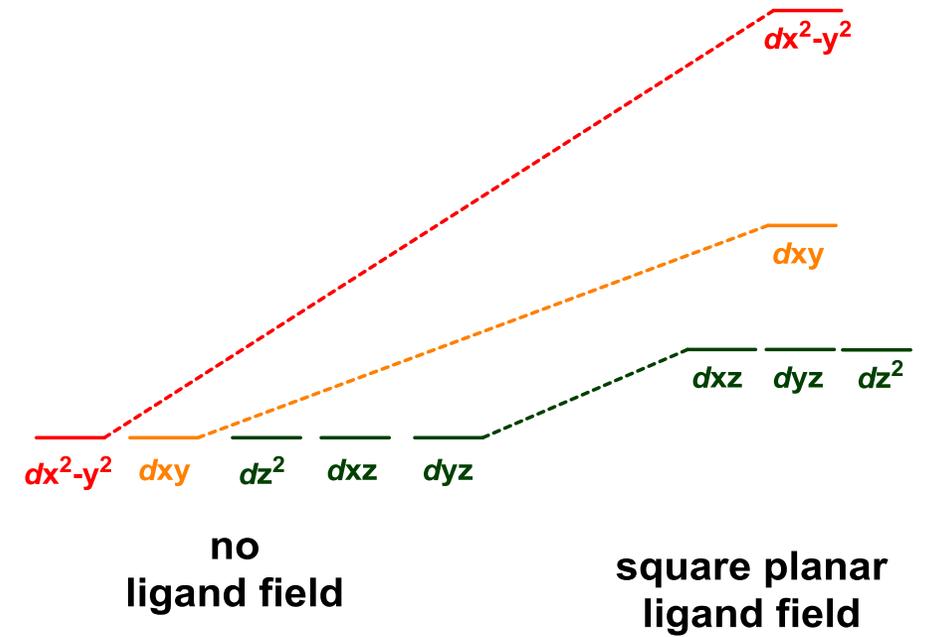
Strong interaction
with ligands



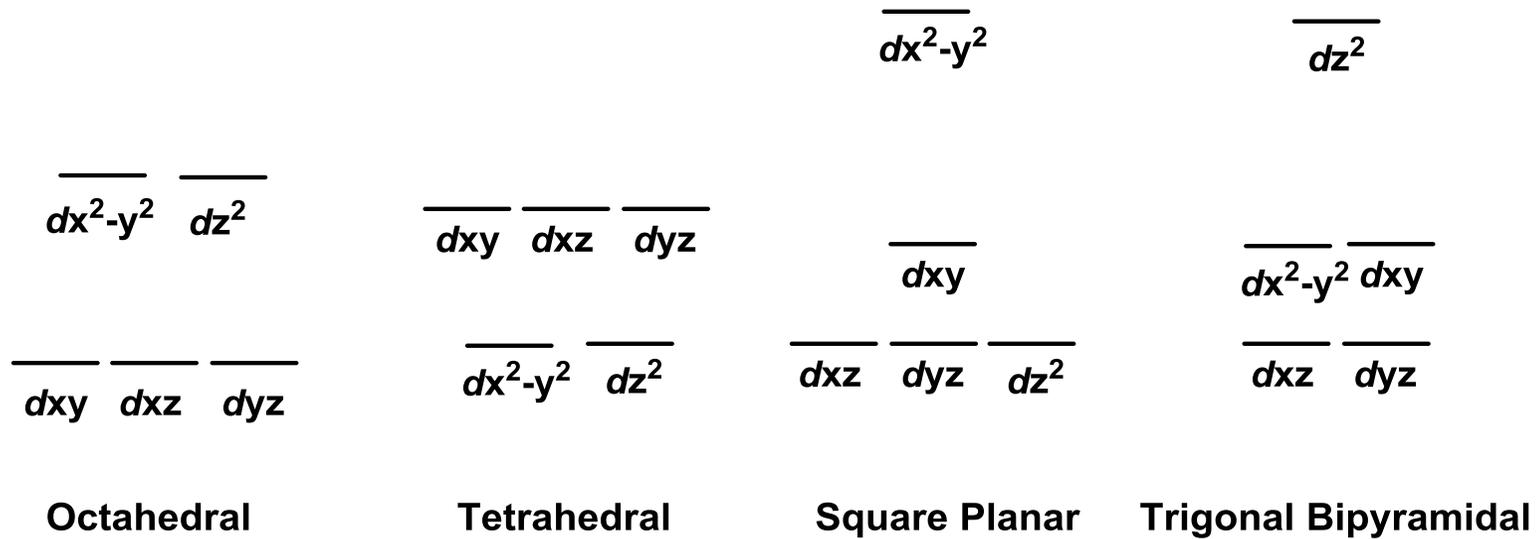
Moderate interaction
with ligands



Weak interaction
with ligands

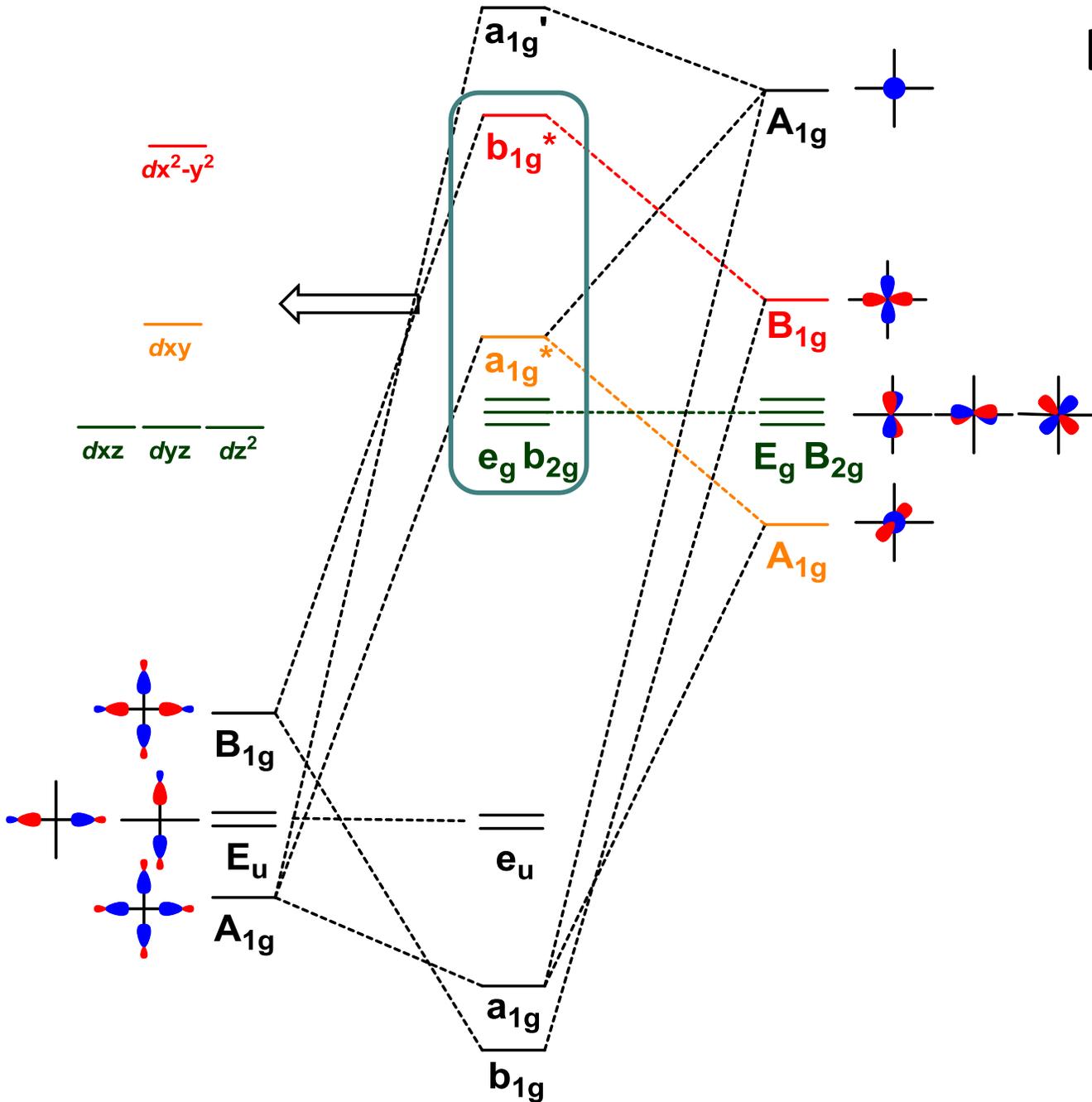


A Few Common Splitting Patterns



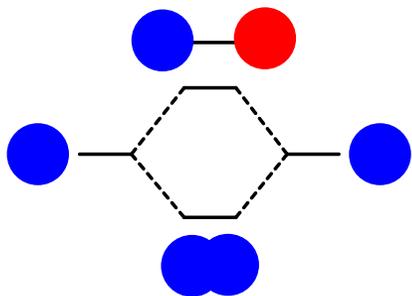
Crystal field diagrams can be derived for various different complex geometries in a similar manner

Ligand Field Theory



- Ligands are not point charges!
- Combinations of ligand orbitals combine with metal orbitals to make a part of bonding and anti-bonding molecular orbitals
- The symmetry and energy of these different combination of ligand orbitals dictate which d -orbitals they combine with
- We can derive a the same splitting of the d -orbitals we obtained via crystal field theory

Polarization of Molecular Orbitals



Atomic orbitals are equal in energy

-Both bonding and anti-bonding molecular orbitals have an equal contribution from each atomic orbital

Examples

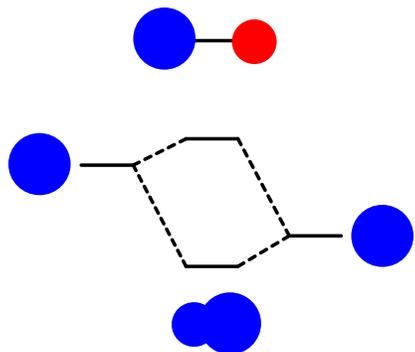
H₂

O₂

N₂

Cl₂

Atomic orbitals are unequal in energy



-Bonding molecular orbitals have a greater contribution from the lower energy atomic orbitals

-Anti-bonding orbitals have a greater contribution from the higher energy atomic orbitals

Examples

HCl

CN⁻

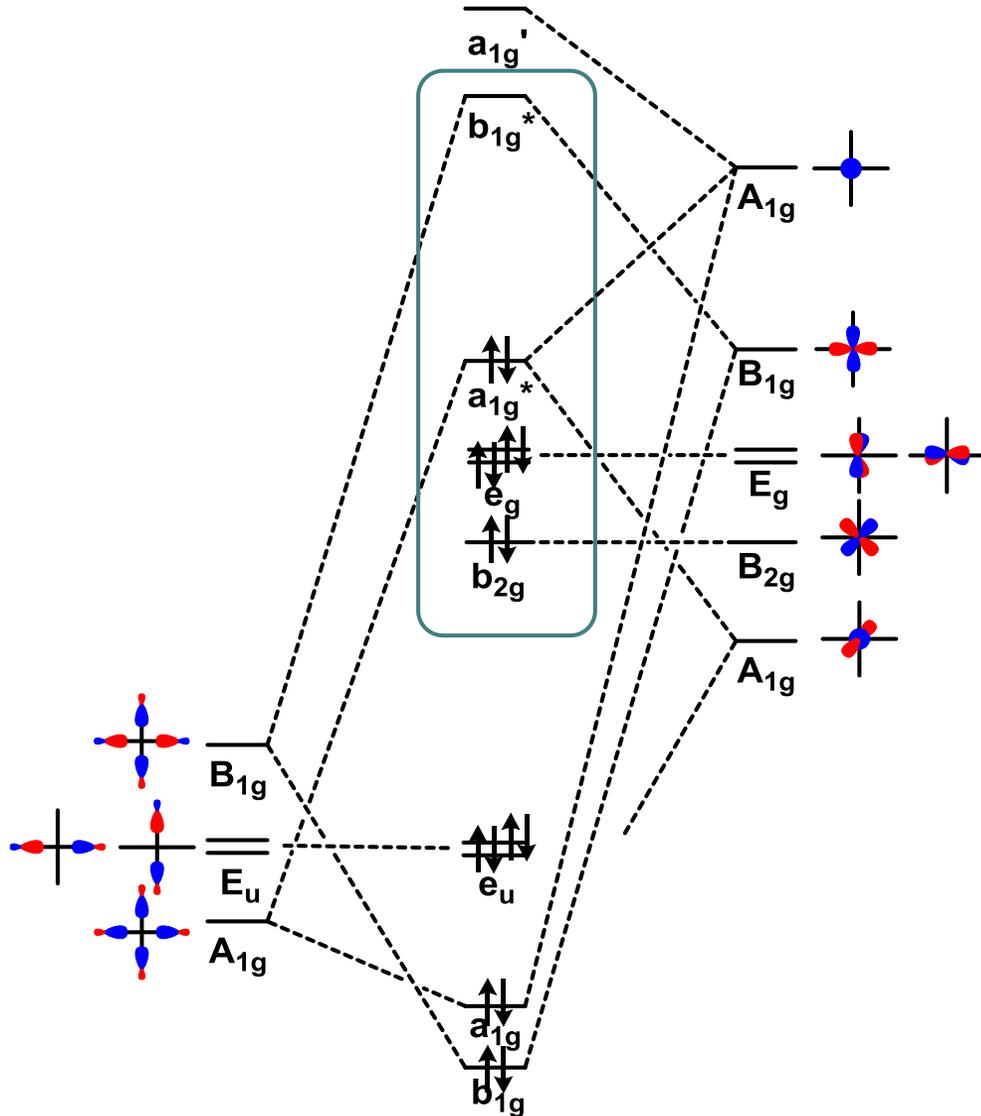
CO

NO

Reactivity of compounds is dependent on the polarization of their molecular orbitals

Inverted Ligand Field

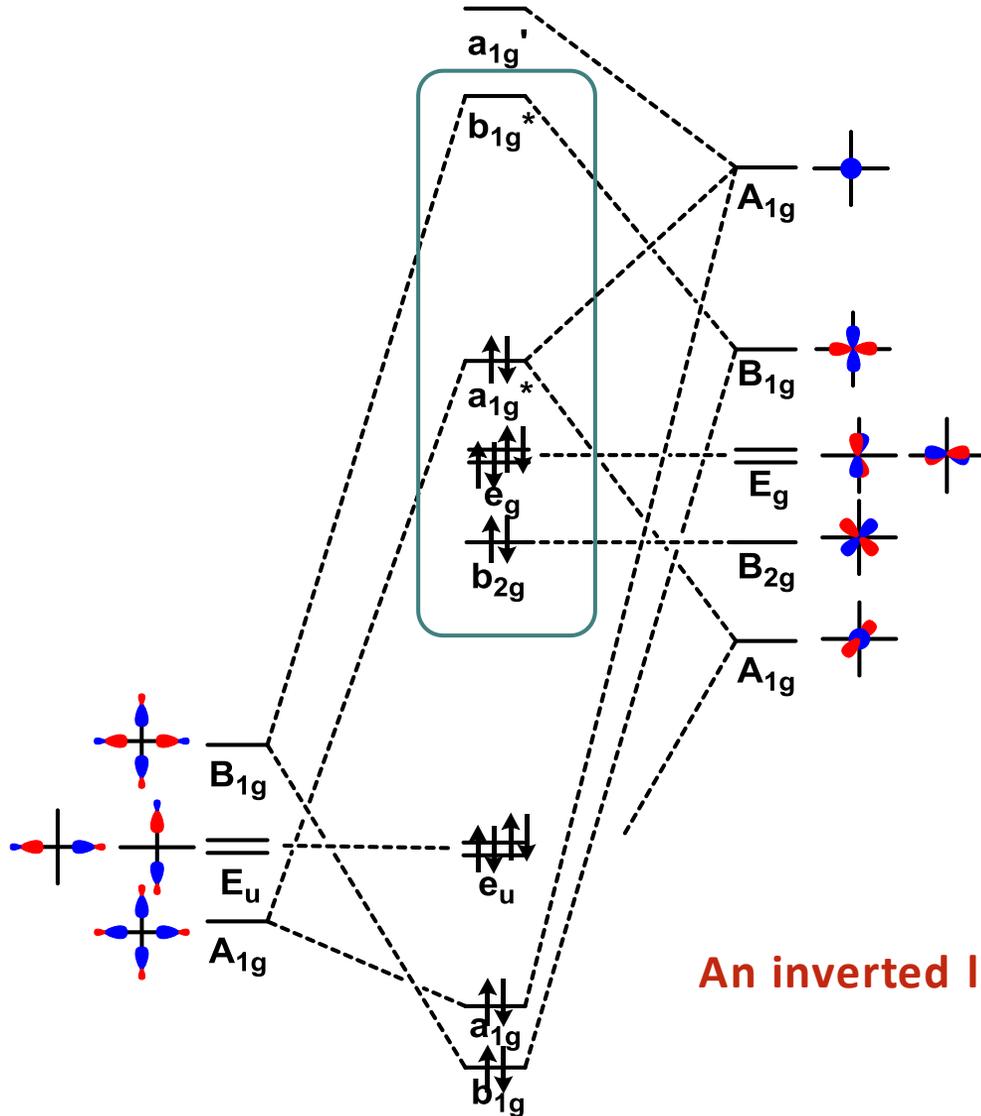
Normal Square Planar Ligand Field Diagram



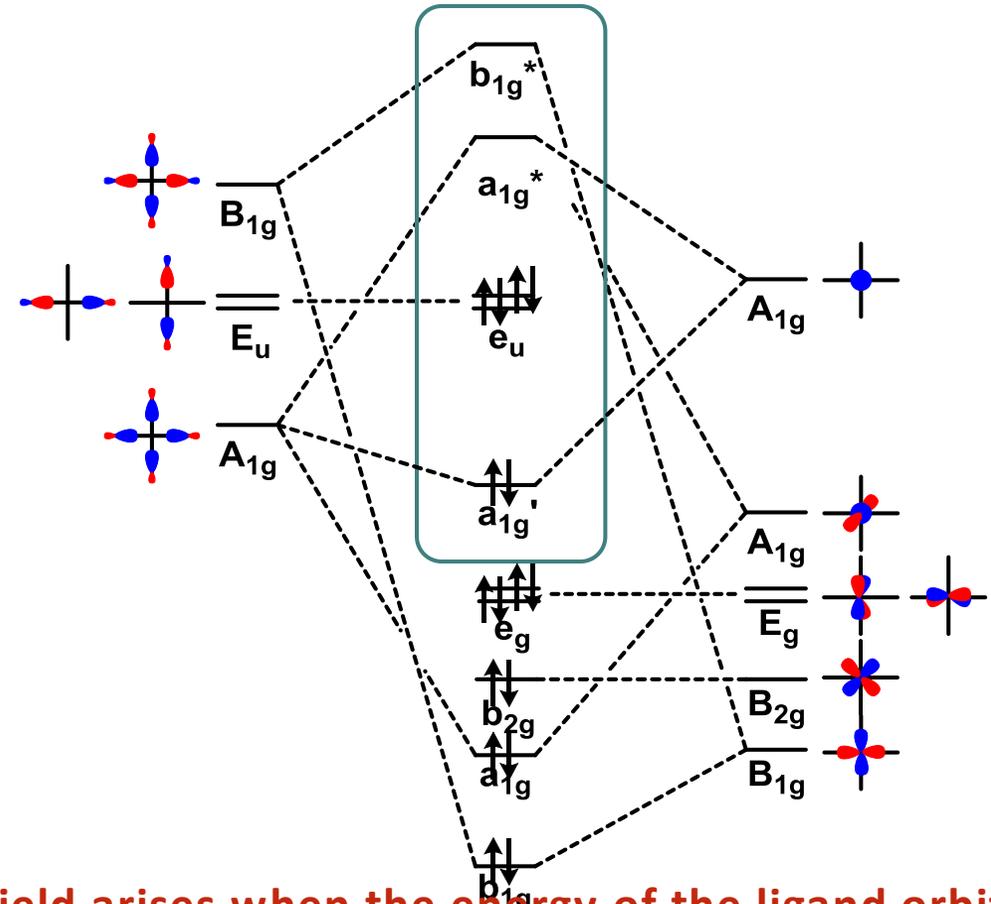
Note the assumption is that the metal orbitals are higher in energy than the ligand orbitals

Inverted Ligand Field

Normal Square Planar Ligand Field Diagram



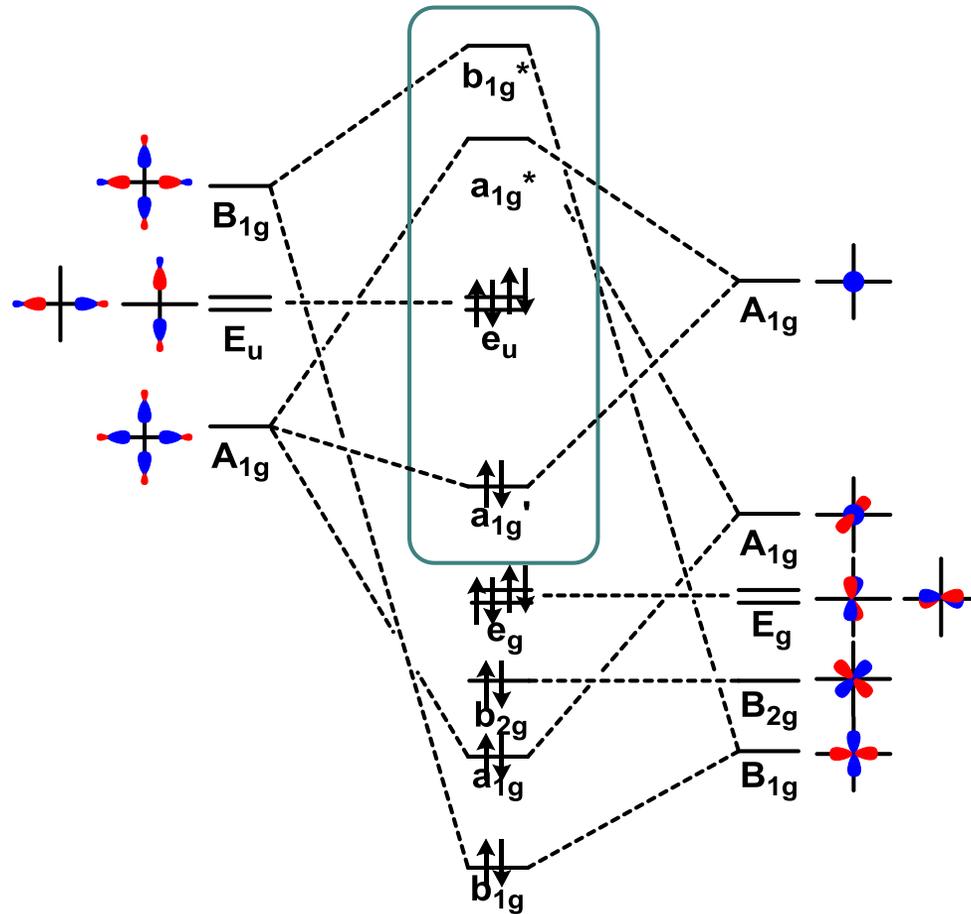
Inverted Square Planar Ligand Field Diagram



An inverted ligand field arises when the energy of the ligand orbitals are higher in energy than the metal d -orbitals

Characteristics of an inverted ligand field

Inverted Square Planar Ligand Field Diagram



-The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is ligand based rather than metal based

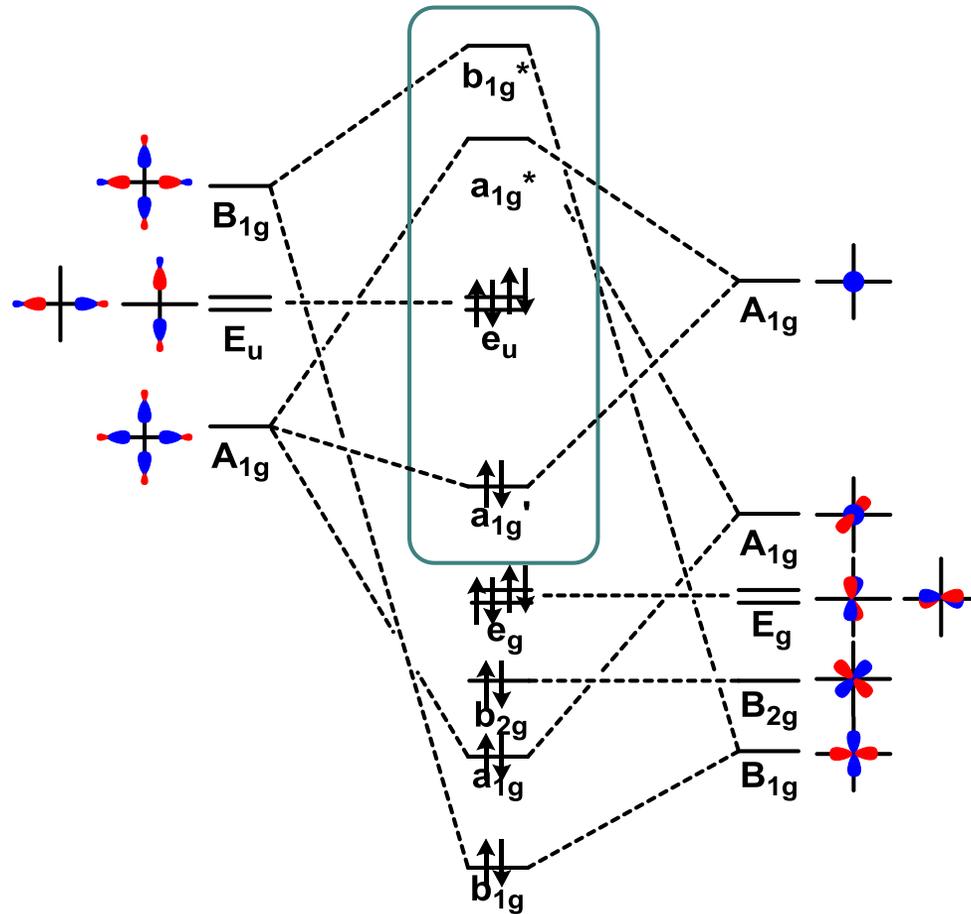
-Suggests reactivity of such complexes might be more dependent on the ligands than the metal orbitals

-The metal is essentially in a d^{10} electronic configuration

-To quote Nate, "They're dope."

What causes an inverted ligand field?

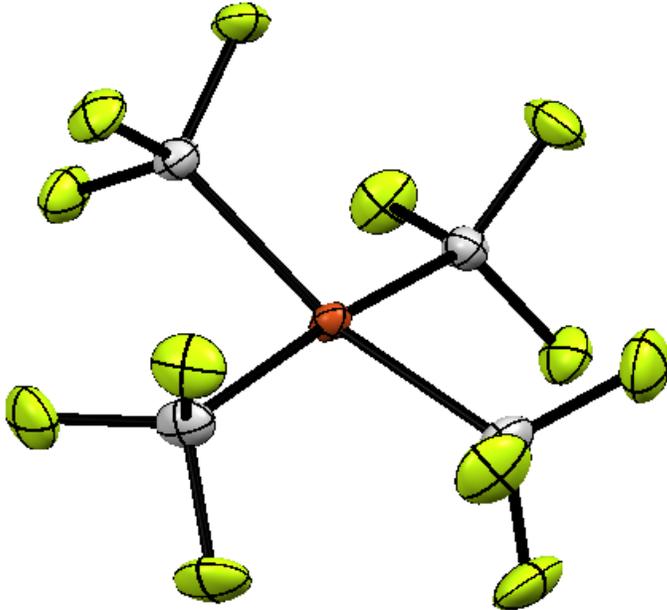
Inverted Square Planar Ligand Field Diagram



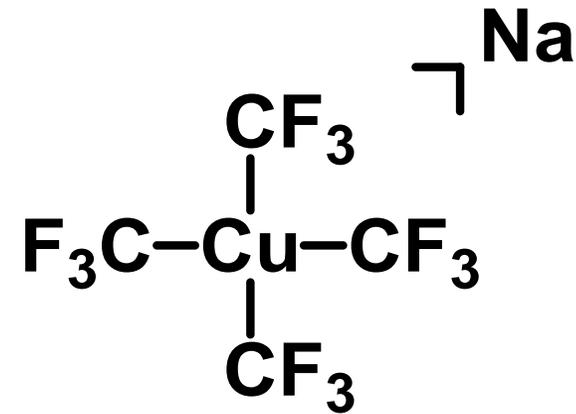
-Highly electronegative ligands increase the energy of the ligand orbitals

-High oxidation state of metal help lower the energy of the metal d -orbitals

$\text{Cu}(\text{CF}_3)_4$ as an example of invert ligand field



=

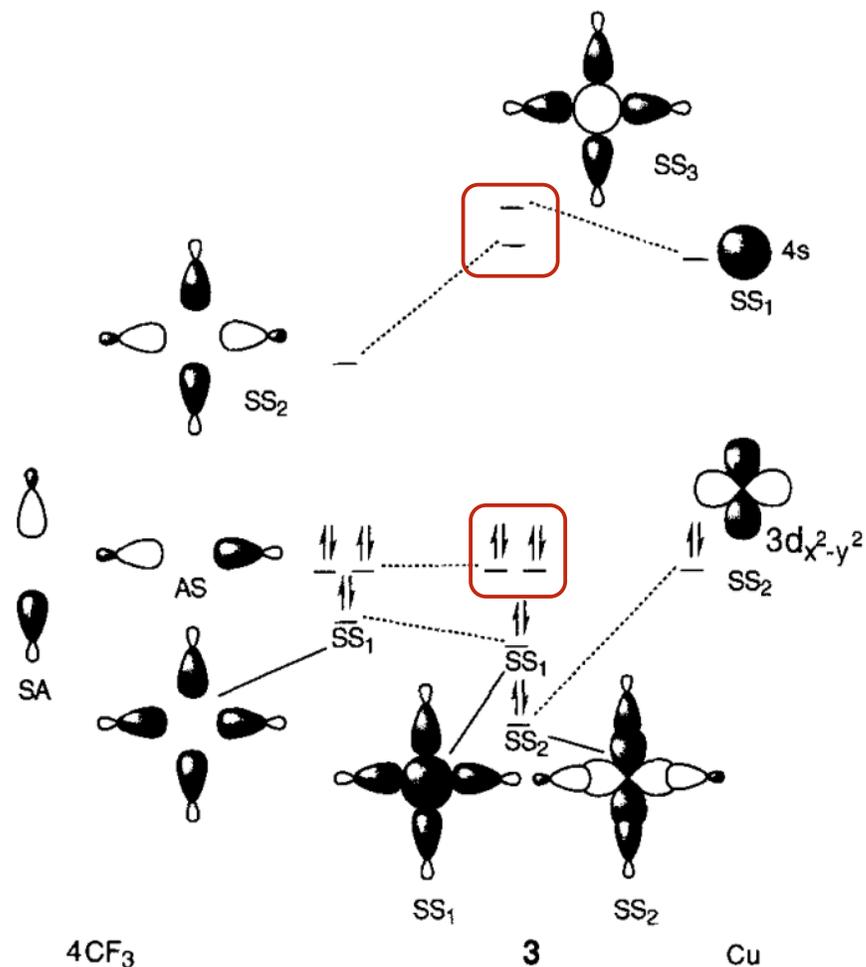


-Formally a $16e^-$ Cu(III) complex

-Geometry is roughly square planar with some distortions due to the size of the CF_3 ligands

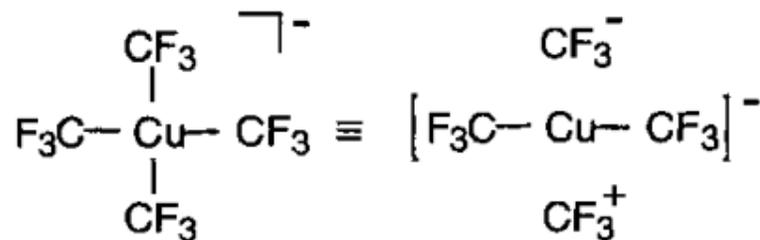
-Remarkably stable for a Cu(III) complex

Some History



Note the HOMO and LUMO are ligand based

-Snyder presented a conversional theoretical paper 1995 describing A formally $\text{Cu(III)(CF}_3)_4^-$ salt as Cu(I) complex with oxidation occurring on the CF_3 ligands rather than the metal center



-The copper atom was calculated to have a partial charge of +0.71, each carbon has a charge of +0.74, and each fluorine -0.39

-The 4 CF_3 units were calculated to contain 25.4 electrons each which is the average of 3 CF_3^- and 1 CF_3^+

James P. Snyder, *Angew. Chem. Int. Ed.*, **1995**, 34, No. 1, 80-81

Academic Fisticuffs

Formal Oxidation State versus Partial Charge—A Comment

Martin Kaupp* and Hans Georg von Schnering

“Evidently, there must be a gross misunderstanding. Snyder has confused two important but fundamentally different concepts: the formal oxidation state, and partial charges as obtained, for example, from population analyses.”

M. Kaupp, H. G. von Schnering, *Angew. Chem. Int. Ed.*, **1995**, 34, No. 9, 986

Distinguishing Copper d^8 and d^{10} Configurations in a Highly Ionic Complex; A Nonformal Metal Oxidation State

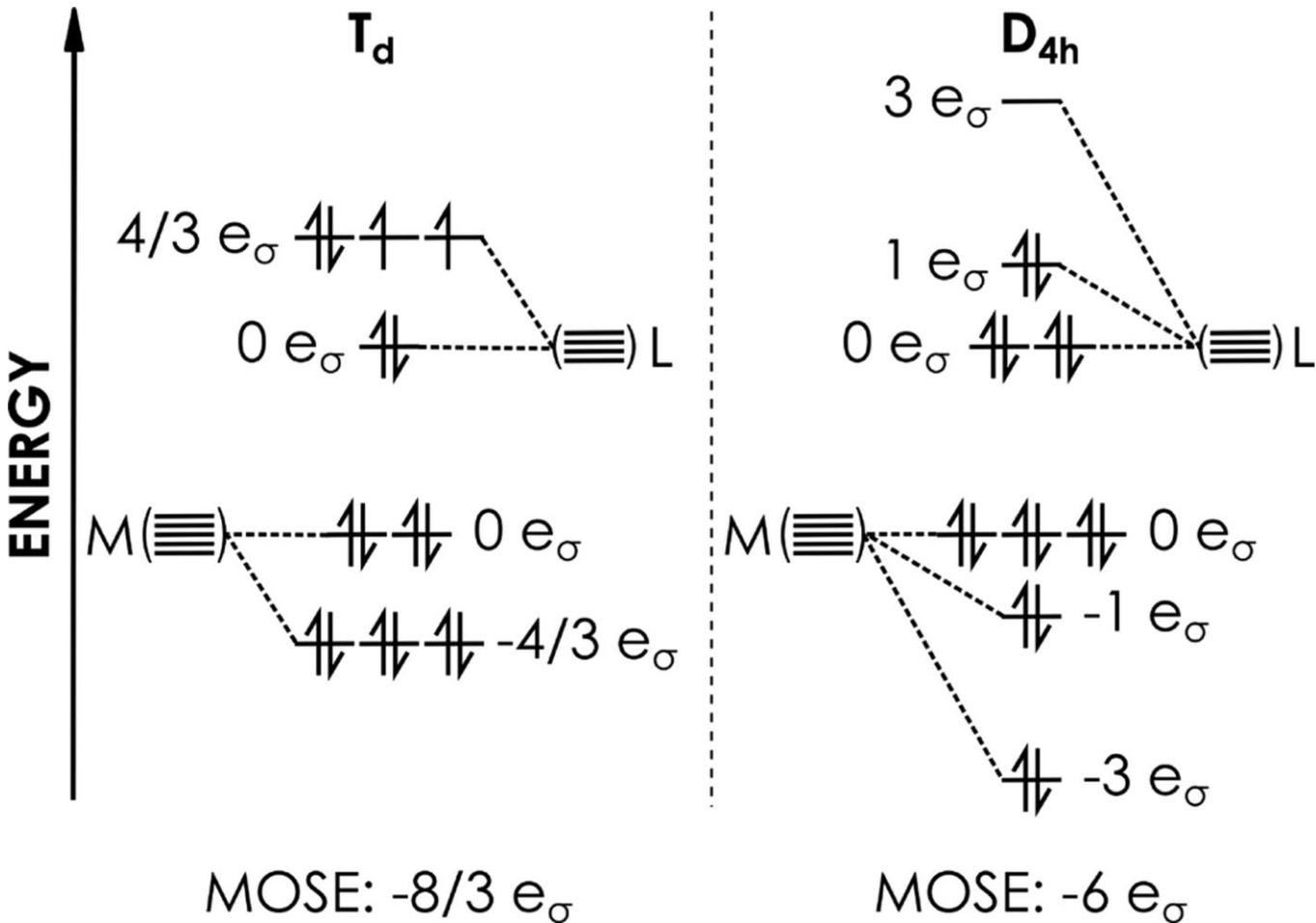
James P. Snyder*

“Since Pauling's introduction of the concept over 40 years ago assignment of *formal* oxidation numbers and oxidation states has proved to be useful for teaching elementary chemical concepts and for cataloguing trends in the periodic table. Nonetheless, apart from isolated monoatomic ions, designation of a formal oxidation state is entirely arbitrary and often accompanied by assumptions as underscored by Kaupp and vonSchnering.”

James P. Snyder, *Angew. Chem. Int. Ed.*, **1995**, 34, No. 9, 986-7

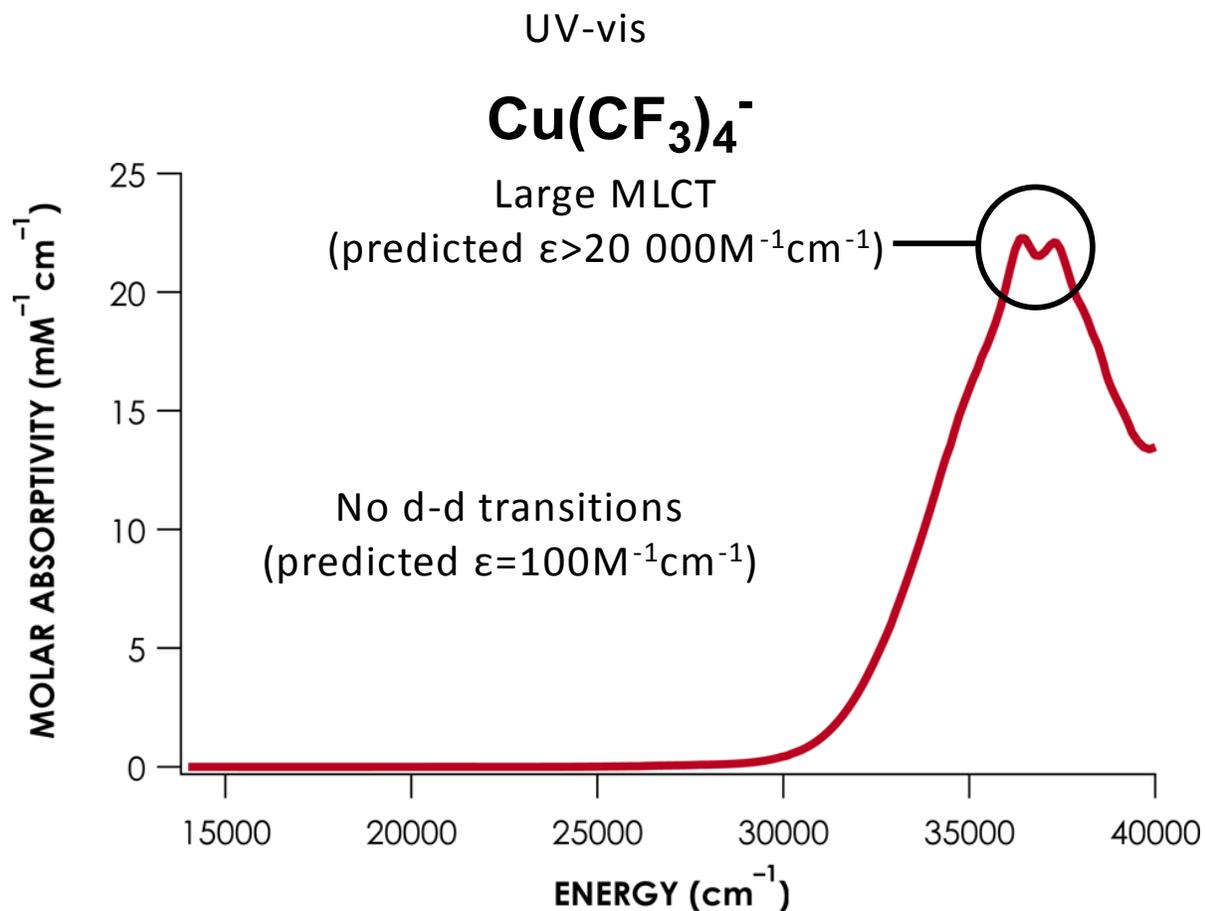
Evidence for inverted Ligand field

Inverted Ligand Field Diagrams for T_d and D_{4h}



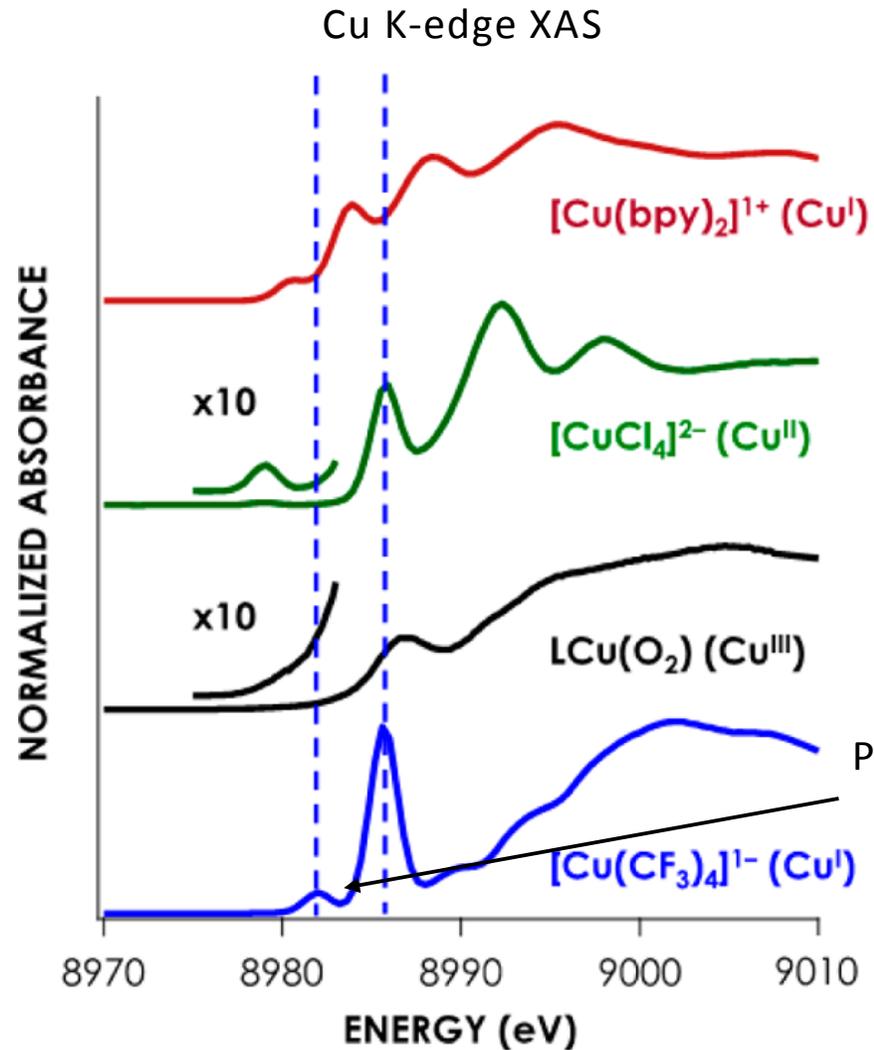
For an inverted ligand field D_{4h} geometry is energetically favorable by $4/3e_\sigma$ for a 16 electron system

Evidence for inverted Ligand field



- no observed d-d transitions expected for a D_{4h} d^8 metal
- having the d-d transition buried under the charge transfer band suggest an very high value for the crystal field splitting

Evidence for inverted Ligand field



- Use of Cu 1s_{2p} RIXS to assign the peak at 8981eV assigned to a Cu 1s → CF₃ σ* transition

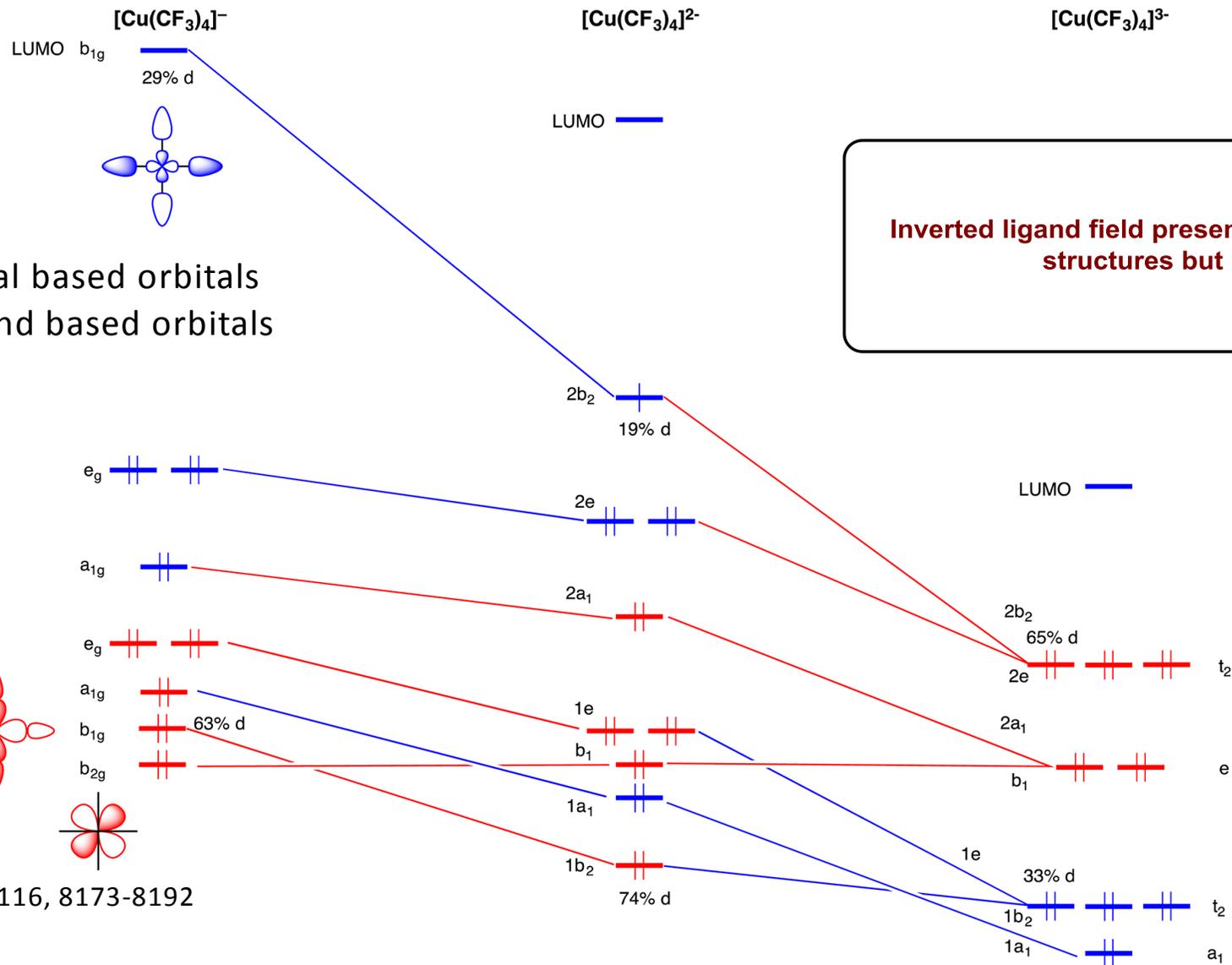
- lack of several spectroscopic features, L_{2,3}-satellite features, that arise from p-d and d-d electron transitions suggest a d₁₀ electronic configuration

Peak at 8981eV typical for Cu(III) centers

K.M. Lancaster *et al.*, *JACS*, **2016**, 138, 1922-31

S. N. MacMillan, and K. M. Lancaster, *ACS Catal.*, **2017**, 7, 1776-1791

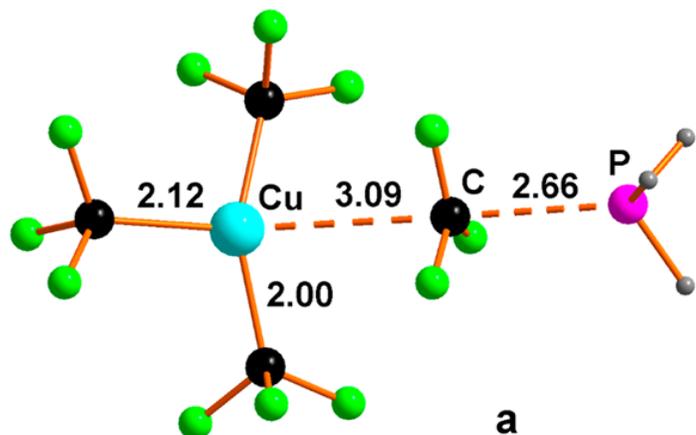
Inverted Ligand Field as a function of Oxidation state



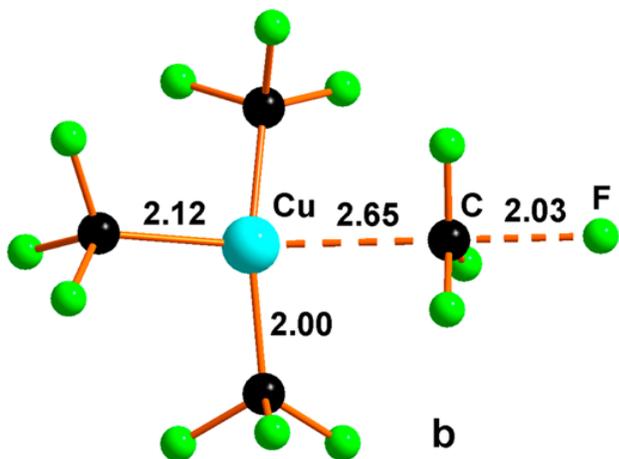
Inverted ligand field present with the Cu(II) and (III) structures but not for Cu(I)

Red is for predominately metal based orbitals
 Blue is for predominately ligand based orbitals

Theoretical Reactivity of $\text{Cu}(\text{CF}_3)_4$



Thermodynamically unfavorable to abstract a CF_3^+ with PH_3 by +47kcal/mol with a kinetic barrier of +79kcal



Thermodynamically favorable to abstract a CF_3^+ with F by -26kcal/mol with a kinetic barrier of +56kcal

“Even if the latter potentially requires drastic thermal conditions to be observed, we are not deterred; computational attempts to lower this reaction barrier, with different substituents, are in progress.”

Conclusions

Inverted ligand field theory suggests an alternative explanation for the spectroscopic properties and chemical reactivity of many high valent metal complexes

Requires the ligand orbitals to be higher in energy than the metal *d* orbitals

- Most common for high valent metals
- typical ligands: CF_3 , F

The unique reactivity of these proposed inverted field compounds is underexplored

